

60 YEARS OF CO ANALYSIS BY NDIR GAS ANALYZERS

Paper# 433

Joseph W. (Bill) Worthington
Technical Support Specialist
ABB, Inc.
843 North Jefferson Street
Lewisburg, WV 24901

ABSTRACT

The Non-Dispersive-Infrared gas analyzer (NDIR) was invented and first used in Germany in the 1930's. This analyzer was the first on-line continuous process gas analyzer. Since that time, many thousands of these analyzers have been produced and used in the fields of combustion, pollution, medical , automotive, chemical, refining, and others. Although this technique has been used to measure more than 100 different gases from ppm to per cent ranges, carbon monoxide (CO) is the most often measured gas by this technique and is discussed as the main example due to its significance in combustion applications. CO is considered a surrogate gas for monitoring the combustion of hazardous air pollutants. Continuous improvements to this technique over the years have made this one of the most successful and versatile techniques for gas analysis. In this paper, a brief survey of the development of this technique is presented together with a short discussion of the theory of operation. Additionally, the state of the art NDIR gas analyzer is shown as the culmination of the 60+ years of continuous development and how this technology is applied to Continuous Emission Monitoring of many fired processes such as industrial boilers, process heaters, furnaces, or other fired processes.

INTRODUCTION

For many years the infrared absorption characteristics of gases have been used for quantitative analysis of gas mixtures. Despite the complexity of the optics and of the detecting system of an infrared spectrometer, this method was and is widely used for a large variety of laboratory and industrial gas analysis problems. Due to the pronounced success of the early spectrometers in performing gas analyses, efforts have been made by a number of investigators to develop simpler infrared equipment that can be more widely applied than the lab spectrometer.(1) This has led to the development of the non-dispersive infrared (NDIR)analyzer that is commonly used today in monitoring carbon monoxide, carbon dioxide, methane, and about 100 other gases. The market for CO analysis dominates other gases and represents approximately 50% of the NDIR analyzers sold today. Additionally and important to the discussion at hand, NDIR is the reference method for determining carbon monoxide concentrations in stationary sources (2) This designation lends

a higher degree of importance to the NDIR analyzer and the state of the art of analysis by this method.

EARLY DEVELOPMENT WORK

It is interesting to note that the scientific theory required to design and understand infrared photometers was more or less completely developed by the time of the 1920's. The earliest spectroscopic work was performed by astronomers. Issac Newton explored the spectrum of sunlight in 1666. In 1752, Thomas Melvill of Scotland first observed spectral lines. William Herschel in 1800 used a prism and a thermometer to learn that the rays providing the maximum heating effect were beyond the visible red rays. Thomas Young used a diffraction grating in 1802 to discern the nature of color in the wavelength of light. 1823, John Herschel described the use of spectral lines to detect small amounts of chemicals August Beer shows in 1852 logarithmic relation to Lambert and the Beer-Lambert law is born. During 1861 James Clerk Maxwell publishes Maxwell's Equations. 1891 has A.A. Michelson inventing the interferometer. Max Plank proposes the quantum theory in 1900, the same year that William Coblenz takes IR spectra of organics. 1926 has W. Heisenberg and E. Schrodinger developing wave mechanics.(3)

The early developers of infrared photometers had the complete theoretical framework to draw from. What was lacking was any type of infrastructure of suppliers, with most having to build most all parts of their equipment. The art that lagged the most was that of electronics. Lee De Forest invented the triode tube, which allowed amplification of signals.(4) Also note that E.C. Wente invented the condenser microphone in 1916, which is an integral part of the Luft type detector.(5) Hans Schmick of Berlin, Germany was granted US Patent 1,691,138, November 13, 1928 for an apparatus for determining the contents of a gas.(6) This was followed by two more patents on similar devices in the next two years.(7)(8). In 1930, Schmick patented the negative filtering method. Apparently this was ignored for many years and was brought back around when interest in infrared equipment increased during World War II.(1) It is interesting to note that this was the basis for the Leeds and Northrop instruments that were used by the Allied Armed Services during WWII. These devices used thermopile type detectors and were offered in ranges of 0 – 1 % CO and were made selective by use of gas filter cells.(1)

The defining moment of nondispersive infrared photometers came from Dr. Erwin Lehrer and Karl Luft, of I.G. Farben, Ludwigschfen, Germany with the development of the Ultrarotabsorptionsschreiber (URAS).(9) This NDIR spectrometer operates according to the principle of negative filtering. Lehrer and Luft were the first to use a microphonic pneumatic detector that also incorporated the sensitizing gas within the detector.(10) Two nickel-chromium coils heated electrically to ca. 1000 K are used as radiation sources. The radiation is modulated by a chopper which is formed like an aperture. A pneumatic detector is used to detect the radiation and its two chambers are connected by a diaphragm capacitor. The chambers are filled with the gas to be measured, usually diluted with N₂. The sample cell is flushed with this gas whilst the reference cell is filled with N₂. If there is absorption of radiation in the sample cell, the gas pressure in the sample chamber of the detector varies and the capacitance of the

diaphragm capacitor also changes at the modulation frequency. The resulting AC voltage is amplified, rectified, and recorded.

FIGURE 1- ERWIN LEHRER (11)



FIGURE 2- KARL LUFT(11)



The energy in the two beams can be made equal by means of an adjustable aperture. The sensitivity can be modified by varying the DC voltage on the capacitor. The range of measurement is determined by the length of the sample cell in any particular case. The interference of accompanying gases is eliminated by filling the filter cells with them. This specifically removes the radiation which they absorb from the two beams. The most important vapors and gases that can be measured with the IR gas analyzer include CO, CO₂, CH₄, C₂H₂, C₂H₆, C₃H₆, NO, N₂O, ethylene oxide, butadiene, acetone, ethyl alcohol, benzene, dimethyl ether, etc. (12)

During the 1930's the chemical industry was in a fast growth period. At the time, Germany was developing infrastructure to supplement its lack of natural resources with chemicals derived from coal that is plentiful. Of the highest priority was synthetic rubber and synthetic petroleum. Technology and measuring techniques were also increasing due to the pressures caused by the expanding chemical industry and the demands of new highly reactive processes. The development work came to the older established plants or works, this because of the longer established working groups that already had the knowledge and experience of the services required by the chemical industry. Numerous measuring procedures were developed and those always were as a germ cell to grow into new devices to serve in the new plants that were being developed and built. Dr. Luft joined IG Farben in 1937, leaving his activities as an assistant of the Physical Institute of the University of Frankfurt and moving into BASF Oppau which promised a versatile and promising sphere of activity ahead. One of the early problems that confronted Dr. Luft was in the new Buna unit of the chemical plant Huls. The manufacturing process used at that time had the danger of explosive butadiene air mixtures. To avoid developing such mixtures, a measurement technique needed to be developed. Butadiene has

strong absorption bands in the infrared, and traditional photometric methods were used to make measurements. However, it was admitted that the photometric methods malfunctioned and the measurement was too strongly affected by CO₂ and H₂O. The use of spectroscopic methods that were more selective were ruled out because of the large expense of this type of instrument. So, the pressure was on to develop a photometer that could solve the selectivity problems. Luft conferred with Erwin Lehrer, who had recently developed a spectrophotometer and they together worked on this problem. After scarcely one year, a first prototype for the measurement of CO in pure H₂ for the ammonia synthesis in the Oppau Plant. The superiority of the photometer over the existing electrochemical measuring instruments was soon demonstrated through fast reliable analysis. It soon convinced the working chemists that the new device with electron tubes could be trusted on such an important operating measurement. Their skepticism and distrust was expected. After the favorable characteristics of the new measurement method were proven, Lehrer and Luft filed for the patent in March 1938 and it was issued in December 1942. In doing the necessary research for the patentability of the technique, extensive literature and patent research had shown that this was not the first use of gas as receivers for infrared radiation. In 1881, Bell, Tyndall, and Roentgen, independently had referred to an optoacoustic effect that in a gas volume with periodically interrupted radiant heat an acoustic wave is created. About the same time that Lehrer and Luft were working on this development, Veingerow and Pfund independently reported application of this effect but more as an unproven curiosity.

FIGURE 3- ORGINAL URAS (10)

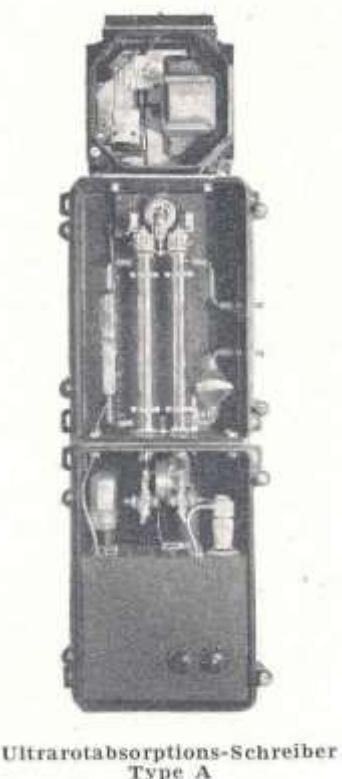
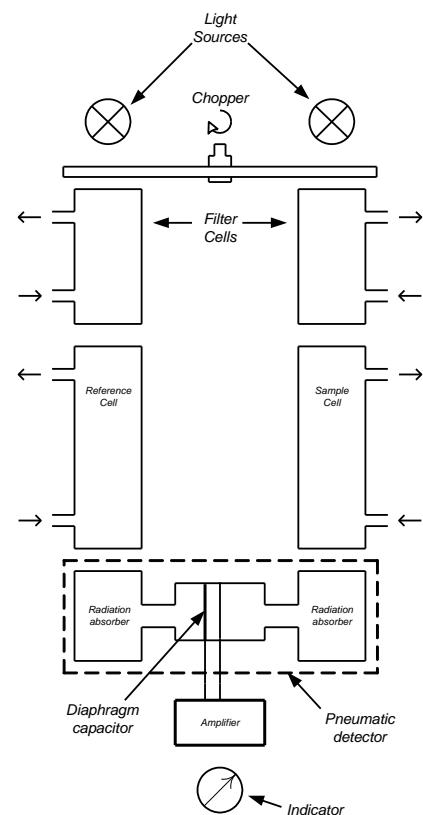


FIGURE 4, URAS OPTICAL BENCH

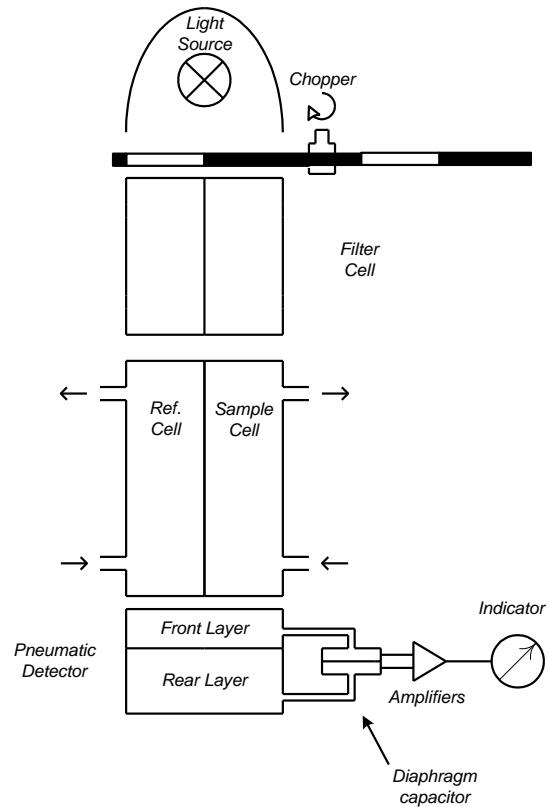


Despite the manufacturing difficulties and the procurement problems of the war economy, several hundred of these gas analyzers were in use in the IG dye industry and other parts of the BASF plants.

Following WWII, Luft went to work in France with ONERA (Office national d'Etudes et de Recherches Aeronautiques, (i.e. the French aerospace research institute) and there worked on further developments of the NDIR techniques. In 1952, the license to produce the Ultrarotabsorptionsschreiber passed from BASF to Hartmann & Braun in Frankfurt including the registered trademark. At the end of 1955 the URAS-1 offered for the measurement of CO, CO₂, or CH₄. Within a short time, 30 gases were possible application gases. Main applications at that time were safety and process measurements in the chemical industry, ambient monitoring for health and explosive detection, flue gases, furnace atmospheres, plant pathology, and medical uses.(13)

Dr. Luft continued development work on the NDIR techniques and in 1957 left ONERA and joined Bergwerksverband GmbH, in Essen, Germany. This is the hard coal mining industry association and conducts research and development to solve the problems of the mining industry. At this time there was a high priority to develop reliable and accurate instruments for the coal mines to measure both CO and CH₄. This led to the two layer receiver principle, which was patented by Dr. Luft in 1955. (14)

FIGURE 5 –OPTICAL BENCH WITH TWO LAYER DETECTOR



The two layer receiver brings several improvements to the NDIR. There are three absorbing possibilities: the sample cell, the front detector layer, and the rear detector layer. The lengths of these chambers must be manipulated so that at the zero point with nitrogen in the sample cell, the IR absorption in the front and rear chambers of the detector cancel and give a zero signal at the zero point. When the sample cell contains the measured component, CO, for example, the centers of the bands absorb more strongly than the flanks. The result of this is that the energy absorbed by the sample is no longer reaching the front layer of the detector, and the resulting pressure in the front layer is reduced. The flanks, or more penetrating rays, continue almost unaffected and still reach the rear layer. In effect, the rear layer of the detector has become the reference cell and the front layer is the measurement cell. This design has excellent zero point stability and also offers other benefits.

Another advantage of the two layer detector is the larger resistance to cross responses. When an interfering gas enters the path, it has a similar effect on both the front and rear layers and the response is nullified. The same is true of dirt on the windows of the sample cell. Clearly, this is not the case in the classic design of the side by side detector.

Without going in depth into the theory of operation of this two layer design, it is important to point out that the real strength of this technique lies with the analysis of simple molecules that have well defined absorption line structure. This is the case with all IR active gases comprised of 2 atoms and most IR active gases comprised of 3 atoms. Gases like CO and CO₂ are perfect candidates for optimum performance. Also, since this technique requires filling the detector with the gas to be measured, there is a requirement that this gas filling is stable over long periods of time, minimum of 24 or 36 months. Some gases like NO₂ and HCl are not stable and thus cannot be filled into the detector. In some cases, a surrogate gas may be available that matches the spectra of the component of interest well enough that measurements may be possible with this approach.

Dr Luft continued his work and filed his final patent (US) in 1976, and left improvements to the next generations.(15)

DEVELOPMENTS FOLLOWING DR. LUFT

A long string of improvements to the NDIR gas analyzer have been made, most have subtle effects on the stability and or sensitivity of the units. For example, one improvement was an optimization of the volumes of the measuring chambers to produce more sensitivity. (16). Another project showed a marked reduction in zero point drift (17) and also incorporated both positive and negative filtering in the same analyzer. The state of the art at this time (1961) could give good results on ranges as low as 0-1000 ppm CO. Currently, the use of gas filter cells for negative filtering continues and is supplemented by the use of interference filters to aid the application specialist meet required performance specifications. These devices allow to remove unwanted IR spectral features to eliminate cross responses. Schaefer in 1973 patented a further improvement to the measuring chamber design to produce a more stable zero point (18). Staab in 1975 demonstrates a method to reduce cross sensitivity (19). Fabinski (20) in 1979 shows how to utilize negative filtering with the sample gas to get a tenfold sensitivity increase, while in

the same year Staab improves upon Schaefer's measuring chamber of 1973 by balancing the centers of gravity of the gas chambers, resulting in a more shock resistant unit.(21) Fabinski in 1981 patents another filtering technique (22) that can also use interference filters. Development continued on this path (23) with the quest always to reduce cross responses. Through continued development, these modest gains do add up to greater performance with ranges of 0-5 ppm CO to be possible today.

PRESSURE COMPENSATION

In earlier days, mechanical means were used to perform pressure compensations and corrections to the gas analyzers. This is demonstrated in the following schematic, figure 6. Element 14 in the figure is a bellows that responds to atmospheric pressure changes and adjusts the shutter 16 to cancel the effect.(24) In contrast, consider the newer approach made possible by newer sensor technology (25). In this manner, the absolute pressure transducer serves to both correct the effects of pressure and to be of use as a flow monitor. This is of course more reliable and robust than the earlier mechanical designs

Figure 6-Mechanical pressure correction

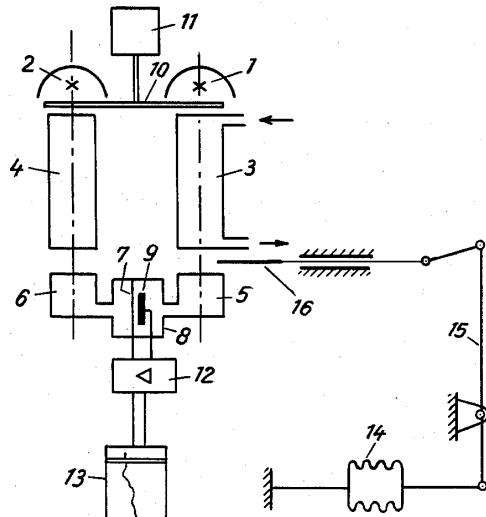
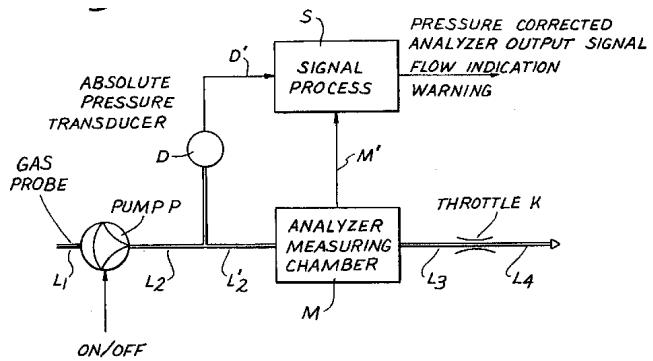


Figure 7-Pressure correction with transducer and signal processing



LINEARITY

Early analyzers had linearizing circuits for this feature. However, other approaches have been realized. For example, Faulhaber et al. (26) in 1976 used a pneumatic detector with 2 diaphragm capacitors in an arrangement that allowed balancing of nonselective changes in intensity that produces a signal that is free from disturbances. Today's microprocessor analyzer allows several methods to be enabled, from form fitting to second and third degree polynominal curve fits.

CALIBRATION

Calibration of the traditional gas analyzer required flowing test gases. This traditional method used test gases that were contained in metal bottles that are usually quite heavy. This meant that recalibration in the field quite expensive and cumbersome. Today, it is possible to perform this function with only nitrogen for setting the zero point and by the use of permanently sealed gas filter cells for spanning of the instrument. A series of inventions were necessary to make this possible. (27) (28) (29) In this process it is necessary to maintain calibration cells in the optical path that contain no absorbing species, usually nitrogen, to maintain optical balance for the normal or measuring operation and the calibration operation. Thus there are two empty gas cells for the normal measurement and two cells, one filled with the species of interest and one with nitrogen. When a calibration is desired, the sample cell is flushed with zero gas, nitrogen is commonly used. After the zero is determined, the cell is inserted that contains the gas of interest and spanning of the analyzer is accomplished. The thickness of the calibration cell is constant at 2 mm. The gas filling concentration is adjusted so that a proper span level is accomplished. Calibration without test gases makes the calibration process more efficient and less costly. Applications of great importance can be calibrated or checked frequently at little additional cost while providing a high confidence level in the performance of the analyzer.

FIGURE 8-CALIBRATION CELL FOR NDIR GAS ANALYZER

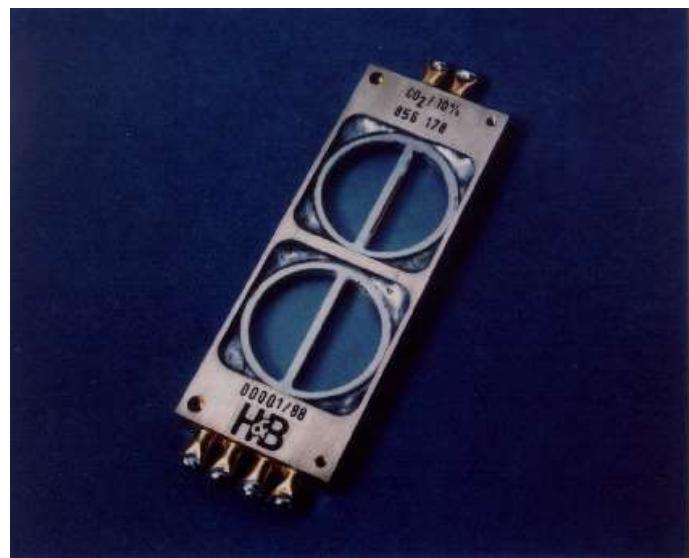
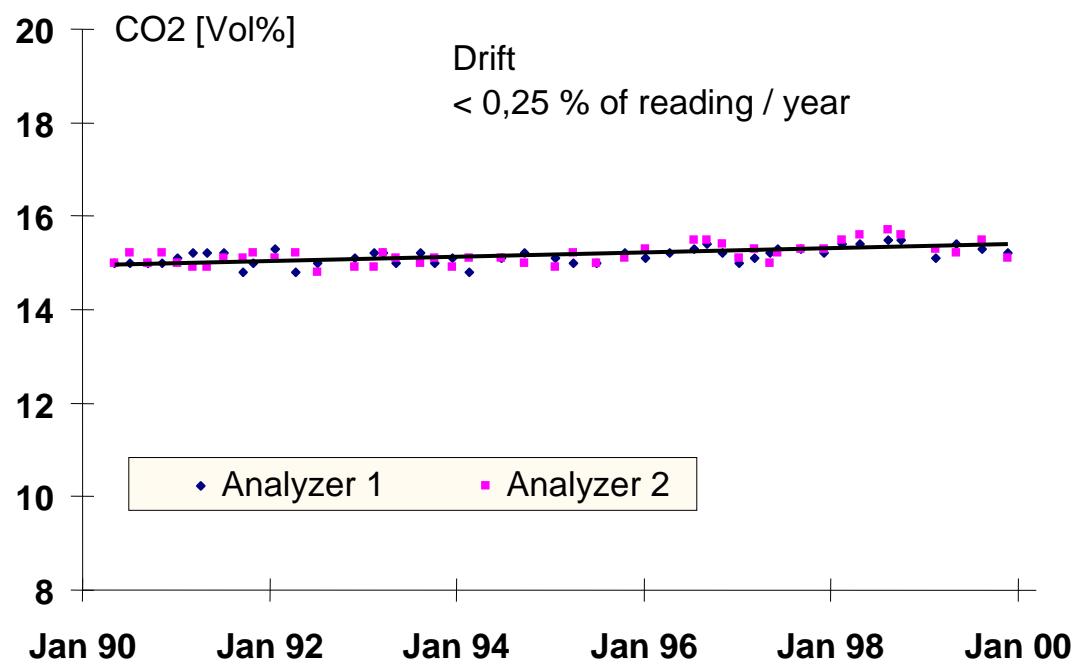


Figure 9: Test Results Demonstrating 10 Year Stability of Calibration Cells



MULTI-COMPONENT ANALYZERS

Another development that has had a large impact on the cost of gas analysis is the multi-component infrared gas analyzer. This has been accomplished by redesigning the opto-pneumatic detector to have an open aperture at the rear, allowing the IR radiation to exit the chamber. A second measuring chamber is then installed so that the IR rays exiting the first detector then enter into the second detector. At the same time, other factors have led to smaller equipment so that now in about one-half of the space previously taken for a single component analyzer can now accommodate an IR gas analyzer to measure four different components. The present arrangement allows two separate beam paths, each fitted with two detectors. An advantage of this approach allows different path lengths in the two beam paths and permits mixing high sensitivity measurements with low sensitivity measurements, for instance like those on combustion sources that require CO₂ measurements in the 10% range and CO measurements in the 100 ppm range or less. (30) (31)

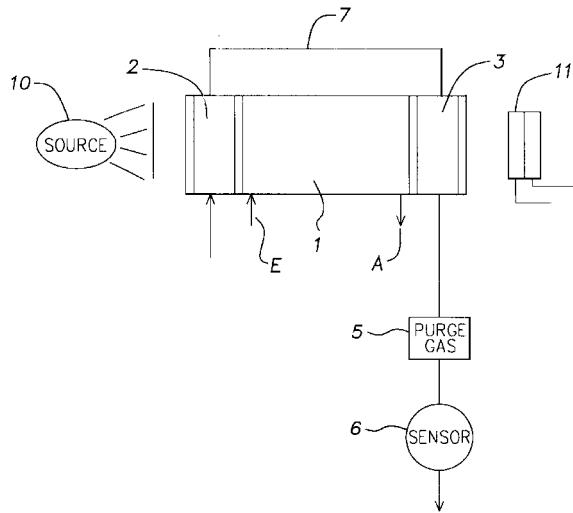
CHEMOMETRIC TREATMENT OF CROSS RESPONSE

Now that the gas analyzer can measure up to four components and has a powerful microprocessor available, it has led to solving of cross responses by chemometric techniques. This is assuming that the interfering components are measured by the analyzer in question. If not, the microprocessor is capable of accepting signals from other measuring devices to perform the chemometric calculations. Thus in the application where CO and CO₂ are measured, it may be more effective to rely on a calculation based procedure than on optical filtering. In addition, as ranges decrease, the effects of cross responses pose a greater threat and the chemometric technique is available as an aid to the application engineer to solve these types of problems.

SAFETY SAMPLE CELLS

The gas analyzers we discuss measure not only toxic gases like CO, but also may be called upon to measure corrosive or combustible gases. In this event and an extra level of safety is merited, the safety cell has been developed (32) (33). The design of the safety cell is such that the toxic and/or corrosive and/or combustible gas sample passes through a gas tight chamber around which a second chamber is arranged that allows the flowing of a purge gas. In the event of a leakage of the toxic sample gas, it must leak into the flowing purge gas which can be vented into an appropriate area.

FIGURE 8-SCHEMATIC OF SAFETY CELL CONCEPT



APPLICATIONS

Safety Monitoring

NDIR gas analyzers have been used for hundreds of applications. In this discussion, we attempt to limit this dialog to carbon monoxide. There are many CO applications, ranging from fire protection in coal storage, coal pulverizers, and other other similar appliances, these are considered to be safety applications and not environmental.

This technique has been widely applied to the measurement of CO in ambient air, tunnels, plants, factories, and other situations. CO in ambient air is an environmental application if performed to satisfy EPA ambient air regulations, otherwise it is also considered a safety application.

Emission Monitoring

Since the reference method for emission monitoring is the Luft-type NDIR (or equivalent) analyzer, this highlights the importance of this method in measuring carbon monoxide. The new source performance standards (NSPS) require CO monitoring for municipal waste incinerators and petroleum refineries. Other sections of the EPA regulations require CO monitoring for boilers, industrial furnaces, process heaters and sewage sludge incinerators (34) (35)

Reference Method Testing

The Luft-type NDIR is designated as the reference method for analyzing CO emissions. This technique must be used for these source tests.

CONCLUSION

The NDIR gas analyzer has an interesting history that begins in 1937 and will continue for years in the future. The measurement levels have consistently dropped from about 0-1000 ppm CO in the 1930's and 1940's until it is now at the 0-5 ppm level. Just as the original invention of this

analyzer was in response to a need, the analyzers of the future will also respond to the needs of the future. Current discussions have CO ranges on some types of combustion equipment at single digit levels. As we progress further it is a certainty that purer gases with less contaminants will be required and the pollution levels will continue to drop. Through a consistent effort of development, the NDIR infrared analyzer will serve the needs of the future generations.

ACKNOWLEDGEMENTS

I wish to thank my friends and colleagues Margareta Ascherfeld and Walter Fabinski for their assistance with the German language and also their insight, knowledge and patience.

REFERENCES

1. Fastie, W.G., and Pfund, A.H., Journal of the Optical Society of America, Volume 37, Number 10, October 1947.
2. Code of Federal Regulations, Chapter 40, Part 60, Appendix A, Method 10- Determination of Carbon Monoxide Emissions from Stationary Sources.
3. Abrahams, Peter; Early Instruments of Astronomical Spectroscopy, <http://home.europa.com/~lescope/histspec.txt>
4. Electronic Design, Vol 24, number 4, Feb 16, 1976.
5. Wente, Edward C., U.S. Patent 1,333,744, issued March 16, 1920.
6. H. Schmick, U.S. Patent 1,691,138
7. H. Schmick, U.S. Patent 1,695,031
8. H. Schmick, U.S. Patent 1,758,088
9. Lehrer. G and Luft K, German Patent 730,478 application March 9, 1938; issued December 14, 1942.
10. K.F. Luft, Zeitschrift fur technische Physik 24, 97 (1943)
11. Becker, Susan; BASF AG EO/P-D102, Personal correspondence
12. Perkanpus, H.H., Encyclopedia of Spectroscopy, VCH 1995.
13. Luft, K.F., Schaefer, W., and Wieglob, G., Technisches Messen 60 (1993) 10, 50 Jahre NDIR-Gasanalyse, Odenbourg Verlag.
14. Luft, K.F., U.S. Patent 2,951,939
15. Luft, K.F., U.S. Patent 3,968,370, issued July 6, 1976.
16. Winterling et al., U.S. Patent 2,844,729, issued July 22, 1958.
17. Hummel et al., U.S. Patent 3,005,097, issued October 17, 1961.
18. Schaefer, W., U.S. Patent 3,725,702, issued April 3, 1975.

19. Staab et al., U.S. Patent 3,925,667, issued December 9, 1975
20. Fabinski et al., U.S. Patent 4,180,732, issued December 25, 1979.
21. Staab et al. U.S. Patent 4,156,813, issued May 29, 1979.
22. Fabinski, U.S. Patent 4,288,693, issued September 8, 1981.
23. Fabinski et al., U.S. Patent 4,306,153, issued December 15, 1981.
24. Schaefer, W., U.S. Patent 3,116,413, issued December 31, 1963.
25. Fabinski et al., U.S. Patent 5,088,313, issued February 18, 1992.
26. Faulhaber et al., U.S. Patent 3,937,962, issued February 10, 1976.
27. Fabinski et al., U.S. Patent 5,003,175, issued March 26, 1991.
28. Fabinski et al., U.S. Patent 5,077,469, issued December 31, 1991.
29. Fabinski et al., U.S. Patent 5,163,601, issued November 17, 1992.
30. Fabinski, U.S. Patent 5,055,068, issued October 8, 1991.
31. Zochbauer et al., U.S. Patent 6,452,182 B1, issued September 17, 2002.
32. Fabinski et al., U.S. Patent 6,484,562, issued November 26, 2002.
33. Fabinski et al., U.S. Patent 6,494,080, issued December 17, 2002.
34. Code of Federal Regulations Chapter 40, Part 266, Appendix IX
35. Code of Federal Regulations Chapter 40, Part 503, Subpart E

KEYWORDS

NDIR, Infrared, Gas Analyzer